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EVALUATION OF A MICROWAVE-INDUCED PLASMA SPECTROMETER FOR TRACE ANALYSIS

William Rudolf Seitz

Environmental Protection Agency
Athens, Georgia

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A low pressure microwave-induced plasma in helium was evaluated as an excitation source for spectrochemical analysis of trace metals in water. The sample was introduced by evaporating a 5-microliter drop of solution on a wire filament and atomizing the solids by the discharge of a capacitor through the filament. The height of the resulting pulse from the photo detector was automatically recorded. Repeatability was about 10% and detection limits were 1 to 25 pg for As, Cd, Hg, and Pb. Slopes of calibration curves depended strongly on matrix and filament effects and the maximum solids loading of the filament was about 5 micrograms.
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ABSTRACT

A low pressure microwave-induced plasma in helium was evaluated as an excitation source for spectrochemical analysis of trace metals in water. The sample is introduced into the plasma by thermal atomization from a wire filament. Although the system is sensitive, calibrations vary in slope as a function of matrix and filament material. Evaluation of the microwave spectrometer was terminated because the instrument required too much further developmental work to make it analytically useful and because other spectrochemical techniques are better adapted to EPA needs.

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SECTION I
CONCLUSIONS

The low pressure microwave plasma spectrometer delivered to EPA needs further developmental work before it can be successfully applied to trace metal analysis in natural waters.

SECTION II
RECOMMENDATIONS

The EPA should sponsor research on other spectrochemical methods for simultaneous multielement analysis. Atomic fluorescence with rapid sequential detection, and RF plasma emission with multiple detectors appear to be the best possibilities at present.

If a reliable atomization system for introducing elements into the plasma is developed, then the low pressure microwave spectrometer should be reconsidered as an emission source for simultaneous multielement analysis.

SECTION III
INTRODUCTION

The EPA needs to be able to analyze for all elements in a water sample simultaneously with sensitivities better than 1 µg/liter. One possible approach is atomic emission spectrometry using a microwave-induced plasma as an excitation source. Microwave-induced plasmas have high electronic temperatures that can efficiently excite emission from elements with high excitation potentials. The plasma itself has relatively few emission lines. An emission source can be adapted to multielement detection by using multiple detectors.

Most work using microwave plasmas for trace metal analysis has been done in argon at atmospheric pressure using a 2450 MHz discharge operating between 25 and 100 watts (1-6). The biggest problem is getting the sample into the plasma. Introducing the sample as a wet aerosol, as in atomic absorption spectrometry, causes background emission from H_2O species and may extinguish the plasma or cause it to be unstable (1). Drying the aerosol before introducing it into the plasma improves analytical performance at the price of greater instrumental complexity (2-4).

Satisfactory analytical performance with good sensitivity has been reported for thermal atomization from loop-shaped filaments (5,6), but other people have failed to achieve satisfactory results with thermal atomization devices (1,3,7).

Although operating a plasma at atmospheric pressure is more convenient, reduced pressure offers several advantages:

- A larger number of gases can be used for the the plasma.
- Greater sensitivity can be achieved at low pressures.
- The problem of metals plating out on the walls of the discharge tube can be avoided.
- Sample introduction by thermal atomization from a filament is facilitated by low pressure.

Good analytical performance has been reported for a low-pressure argon plasma into which the sample is introduced as a partially desolvated aerosol (8). Introducing dry aerosol into a low pressure plasma has not been reported and would probably be difficult. Poor reproducibility was observed for thermal atomization of Hg from a copper filament into a low-pressure argon plasma (7).

In this report a microwave plasma emission spectrometer designed to operate at low pressures using thermal atomization from a metal filament is found to be subject to matrix effects that make it unsatisfactory for water analysis.

SECTION IV
EXPERIMENTAL

APPARATUS

The microwave plasma spectrometer was built on contract by Monsanto Research Corporation, Dayton, Ohio, and delivered to the EPA at the conclusion of the contract period. The spectrometer is described in detail in the final report on the contract (9).

The spectrometer operates at low pressure with sample introduction by thermal atomization from a heated metal filament. The plasma is confined in an 8 mm i.d. quartz tube. The position of the plasma relative to the viewing port can be varied. Normal operating conditions for the plasma were 30-40 watts power, 2-3 mm pressure and a flow rate of approximately 250 cm^3 helium/minute.

A 0.025-cm. diameter Ta filament is located about 2 cm above the plasma. The filament geometry recommended by Monsanto was an acute V. A drop of sample is placed at the point of the V. After the water evaporates leaving solid on the probe, the solid sample is thermally atomized by discharging a 0.21-farad capacitor charged to 7-10 volts through the filament. In other thermal atomization systems, the filament heating current is controlled by a rheostat (5-7). The purpose of using a capacitive discharge is to increase sensitivity by introducing the entire sample into the plasma over a

very short time period. Emission-peaks viewed on the oscilloscope had a half-width of less than ten milliseconds.

The emission signal is too fast to be recorded on a strip chart recorder. Instead, a peak-reading circuit holds the peak value of the emission signal, which is printed by a digital printer.

The spectrometer can be programmed to do the following operations automatically in sequence at preselected time intervals:

(1) Turn on carrier gas (helium)

(2) Evaporate sample drop on filament by passing current (0-1 A) through the filament

(3) Reduce the pressure

(4) Turn on plasma

'5) Atomize sample

(6) Print out peak height

(7) Turn off and vent system

PROCEDURES

Measurements were performed by removing the sample probe with the filament from the spectrometer, placing a five-microliter drop on it, and replacing the probe in

the spectrometer. The automatic program was then initiated. Analysis time was eight minutes. Approximately five minutes were required to evaporate five microliters at the maximum desolvation current.

SECTION V
RESULTS

SENSITIVITY

The plasma spectrometer built by Monsanto provides greater sensitivity than other microwave plasma spectrometers previously reported (1-8). Table 1 lists detection limits for the Monsanto spectrometer (9). The superior excitation efficiency of the low-pressure helium plasma and the use of a capacitive discharge to atomize the sample both contribute to the increased sensitivity, but the relative contributions of each are not known.

CALIBRATION CURVES

Table 2 lists the slopes of log concentration-log peak height calibration curves under various conditions. The slope is a function of filament material and matrix. Since the slope changes with matrix for a given filament material, the problem is probably with the process of evaporating the drop onto the filament rather than with the plasma itself. This effect is reflected in the data from Monsanto and was confirmed for Cd in river water vs. Cd in deionized water. Because of this, natural water samples cannot be analyzed using calibration curves prepared in deionized water.

The sample properties that cause this effect are unknown. It could be related to surface tension,

Table 1. DETECTION LIMITS OBSERVED FOR THE MICROWAVE EMISSION PLASMA SPECTROMETER USING A LOW-PRESSURE HELIUM PLASMA (9)

Metal	Detection Limit (µg/liter)
As	5
Cd	0.2
Hg	0.5
Pb	5

Monsanto projects that these detection limits can be reduced 10X by optimization.

Table 2. SLOPE OF LOG PEAK HEIGHT vs. LOG CONCENTRATION FOR SEVERAL METALS AS A FUNCTION OF FILAMENT MATERIAL AND MATRIX

Metal	Matrix	Filament	Concentration Range (mg/ℓ)	Slope of Log Pk. Ht. vs. Log Concentration	Reference
Hg	Hg Metal	Introduced as vapor	5x10-5 to 2.7 x10-3 µg/cc	1.00	9
Hg	Deionized H_2O	W	0.01 to 10	0.42	9
Hg	Deionized H_2O	Ta	0.01 to 10	1.09	9
Hg	Maumee River Water	Ta	0.010 to 5	1.23	9
Pb	Deionized H_2O	Ta	0.1 to 10	0.53	9
Cd	Deionized H_2O	W	0.01 to 10	0.61	9
Cd	Deionized H_2O	Ta	0.002-2	0.67	
Cd	Oconee River Water	Ta	0.002-2	1.00	
As	Deionized H_2O	W	0.1 to 10	0.82	9

solubility of the metal to be analyzed, dissolved solids content of the sample, or the tendency of the metal to adsorb on the filament. It may be possible to find a "constant matrix" that could be added to both standards and sample to suppress the effects leading to changes in the slopes of log-log calibration curves with matrix. However, because the origin of this effect is not understood, it is very difficult to predict what, if anything, might be a successful constant matrix.

EFFECT OF DISSOLVED SOLIDS

In looking for a constant matrix it was found that when water containing a high concentration of dissolved solids is evaporated onto the filament, discharging the capacitor through the filament causes the plasma to momentarily shrink in size, interfering with the emission measurement. Apparently firing the filament generates a small cloud of gas that interferes with the normal helium flow. Five microliters of 10^{-2} molar solution deposited on the filament would produce 0.4 cm^3 of gas at 2 mm pressure and room temperature, assuming 1 gas molecule per 1 solid molecule. This volume of gas would be expected to produce the observed effect.

This effect limits the low pressure microwave spectrometry to freshwater samples and restricts the possibilities for a constant matrix that might lead to satisfactory analytical performance.

PRECISION

Monsanto reports 2% standard deviation in peak height measurements at 10^{-10} grams of sample in 5 microliters (0.02 mg/ℓ). Because log peak height-log concentration curves have slopes less than one, 2% standard deviation in peak height corresponds to a larger standard deviation in concentration.

Satisfactory precision (about 10%) was obtained only when the drop of sample did not wet the filament. Immediately after firing, a Ta filament is wettable by aqueous solutions. After standing in air for 10-60 seconds however, it is no longer wettable.

The plasma length at each firing varied 2 mm out of a total plasma length of 8 cm. Since intensity of the emission signal varies with position in the plasma, this leads to a change in peak height. This was corrected by adjusting the plasma power to compensate for any changes in plasma length.

SECTION VI
DISCUSSION

The evaluation of the microwave plasma spectrometer was terminated earlier than originally planned for the following reasons:

- It was evident that the thermal atomization system for introducing sample into the plasma needed to be modified so that emission would be independent of matrix. It was uncertain whether an improved atomization system is feasible and how long it would take to develop.

- Other spectrochemical methods, which have demonstrated performance, require less time for analysis and can be readily automated, better fill the EPA need for simultaneous multielement analysis. Pulsed source atomic fluorescence determines up to 12 elements in less than one minute and has already been automated (18). RF plasma emission spectrometry determines over 20 elements in less than one minute and can be readily automated (19). The microwave spectrometer requires 8 minutes per analysis and is not readily automated. Table 3 summarizes work on spectrochemical multielement analysis using flame and plasma excitation. References 11-18 come from a review article by Busch and Morrison that gives a detailed analysis of the problems and possibilities for multielement flame spectroscopy (10).

TABLE 3. SURVEY OF FLAME SPECTROPHOTOMETRIC APPROACHES TO SIMULTANEOUS MULTIELEMENT ANALYSIS (AA=ATOMIC ABSORPTION, AF=ATOMIC FLUORESCENCE, FE=FLAME EMISSION)

Reference	Technique	Elements Analyzed Number, Identity and Detection Limits (mg/l)	Principle Used to Achieve Multielement Capability	Area of Application
11	FE	Five Na(0.002), K(0.2), Ca(0.02) Mg(0.6), Sr(0.02)	Multiple slit, multiple detectors	Clinical
12	AA FE	Six Cr, Ni, Mg by AA K, Ca, Na by FE	Multiple detectors; light from hollow cathode lamps optically combined into one beam	
13	AA FE	Four Na(0.06), K(0.4), Ca(0.08) by FE Mg(0.02) by AA	Rapid spectral scanning	Clinical
14	AF	Four Ag(0.002), Cu(0.003) Fe(0.1), Mg(0.001)	Mechanical synchronization between pulse to hollow cathode lamp exciting fluorescence and positioning of different interference filters for each element in front of photomultiplier	Soil Extracts
15	AF FE	Six Ca(0.007), Cu(0.01), Mg(0.004) Mn(0.01), Zn(0.007) by AF K(0.007) by FE		
16	AF	Four Zn(0.001), Cd(0.001) Co(0.01), Ni(0.02)	Excitation by two dual element electrodeless discharge lamps; rapid spectral scanning	
17	AF FE		Use of Vidicon detector (an optical multichannel analyzer)	
18	AF	Twelve Zn(0.02), Cd(0.05), Ni(0.07) Fe(0.05), Mn(0.03), Mg(0.001) Cu(0.01), Cr(0.5), Ca(0.001)	Programmed sequential monochromator synchronized with pulse to hollow cathode lamps	Orchard Leaves, Urine
19	RF Plasma Emission	Twenty	Multiple slit, multiple detectors	Water
20	DC Plasma Emission	Ten	Modulation of different wavelengths at different frequencies with selective demodulation	

- The principle advantages of the low-pressure microwave plasma spectrometer are not useful to the EPA. The small sample size requirement (1-10 microliters) is not significant for water analysis because more sample is usually available The improvements in sensitivity for single element analysis can also be obtained by flameless atomic absorption, which does not have the same problem with calibration curve slopes as low-pressure microwave spectrometry.

If the operational problems are solved to make low pressure microwave plasma emission spectrometry a reliable analytical technique, it will be a significant advance in analytical methodology because it will combine the advantages of flameless atomization (sensitivity and small sample size) with the advantages of working with emission rather than absorption (no need for a light source and easier adaptation to multielement analysis). However, fundamental instrument development is not normally a mission of the NWCCRP. If a satisfactory thermal atomization system for introducing the metal sample into the plasma is developed, then the microwave plasma spectrometer should be reconsidered. The improved thermal atomization system must inject the sample into the plasma rapidly. Otherwise broadening of the emission peak will reduce sensitivity and the principle advantage of the low pressure microwave plasma spectrometer will be lost.

This evaluation of the low-pressure microwave plasma emission spectrometer is restricted to metal analysis in aqueous samples requiring atomization. Microwave plasmas have been successfully used with vapor phase samples, e.g., arsenic analysis as AsH_3 gas (21) and detection of GC effluents (22-25).

SECTION VII

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